

OFFICE OF NAVAL RESEARCH

GRANT : N00014-89-J-3062

R&T Code 3132084

Technical Report No. 38

Synthesis and Applications of Linear Step Growth Oligomers and Polymers of Precisely
Controlled Length and Constitution. A Review

by

James M. Tour

Accepted for Publication in

Trends in Polym. Sci. **1994**, 2, 332.

Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

June 7, 1995

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.

DTIC QUALITY INSPECTED 5

19950705 049



REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 6-7-95		3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE Synthesis and Applications of Linear Step Growth Oligomers and Polymers of Precisely Controlled Length and Constitution. A Review				5. FUNDING NUMBERS G- N00014-89-J3062 R&T 3132084	
6. AUTHOR(S) James M. Tour				Kenneth Wynne	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry and Biochemistry University of South Carolina Columbia, SC 29208				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000				10. SPONSORING/MONITORING AGENCY REPORT NUMBER 38	
11. SUPPLEMENTARY NOTES Trends in Polym. Sci. 1994, 2, 332.					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Oligomers and polymers of precisely defined length and constitution are not new synthetic targets, but modern synthetic reactions have provided access to novel and diverse structures. These extremely well-defined compounds serve as models for their higher, less well-defined homologues, and they can reveal important information relating to physical, electronic and optical responses in polymers. Described here are the modern synthetic, and biochemical approaches to linear oligomers and polymers of near exact molecular composition. The current and potential uses of these interesting compounds is outlined.					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
				20. LIMITATION OF ABSTRACT UL	

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std Z39-18
298-102

Syntheses and Applications of Linear Step Growth Oligomers and Polymers of Precisely Controlled Length and Constitution

James M. Tour

Department of Chemistry and Biochemistry

University of South Carolina

Columbia, South Carolina 29208

USA

Phone: 803-777-9517

FAX: 803-777-9521

Email: tour@chem.chem.scarcolina.edu

Accession For	
NTIS	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

Oligomers and polymers of precisely defined length and constitution are not new synthetic targets, but modern synthetic reactions have provided access to novel and diverse structures. These extremely well-defined compounds serve as models for their higher, less well-defined homologues, and they can reveal important information relating to physical, electronic and optical responses in polymers. Described here are the modern synthetic, and biochemical approaches to linear oligomers and polymers of near exact molecular composition. The current and potential uses of these interesting compounds is outlined.

Due to the statistical nature of polymerization processes, most synthetic reactions that afford polymeric compounds generate polydisperse materials. Prior to the high polymer limit, such heterogeneity is often beneficial since it can serve to retard crystallization. On the other hand, the generation of monodisperse materials can also be of enormous importance, and much effort has concentrated on the formation of near homogeneous vinyl polymers. Step growth monodisperse polymers are far less commonly observed, though they have been synthetic targets for over 30 years¹. Outlined here will be modern synthetic approaches to step growth oligomers and polymers that possess precisely controlled lengths and molecular constitutions. The current and potential applications of these new compounds will be presented. The nonlinear dendritic-type polymers will not be discussed and the area has recently been extensively reviewed^{2,3}. Likewise, extended structures prepared by Langmuir Blodgett techniques, most often resulting in non-covalently linked arrays, will not be discussed.

The point at which one refers to a homologous series as an oligomer as opposed to a polymer has been controversial. In fact, different authors have designated values of 20 monomer units, 1000, 6000, or 10,000 Da, as the oligomer/polymer distinction point⁴. The reasons for such demarcations are synthesis- or property-related and no definitive segregation points will be inferred in this coverage of the topic. Nevertheless, the preparation and utilization of oligomeric and polymeric frameworks that are monodisperse is becoming tremendously important in fields ranging from electronics to biology, and we stand to gain much chemical and physical insight by this pursuit.

Why study oligomers and polymers with precisely controlled lengths?

Oligomers and polymers of specific controlled length serve as excellent models for their corresponding polydisperse macromolecular materials^{4,5}. These precise models often provide specific information concerning the solution, electronic, photonic, thermal, and morphological properties of their higher homologues. They also serve as useful models for interpreting structural and conformational properties of a polymer. When does an oligomer begin responding like a polymer for a specific function? For example, at what degree of polymerization does a conjugated polymer start responding like a conducting polymer? By building a series of oligomers and determining their photonic response trends, can we assess the required minimum degree of polymerization needed to attain a desired optical response from a polymer? Can we learn about polymer conformations in solution by studying the responses of a family of well-defined, spectroscopically simple, smaller structures? Is there detailed X-ray structural data of well-defined oligomeric systems that can be used to predict morphological patterns of bulk polymeric materials? The answer to these questions, and far more, can indeed come by an analysis of precisely defined oligomers and polymers. Therefore, exact data can be obtained that relates chain length and conformation to physical, electronic, and optical phenomena.

In addition to these well-defined systems serving as models for higher homologues, there exists distinct advantages to utilizing precisely controlled length, size, and shaped compounds. For example, macromolecules with definitive architectures can serve as hosts for guest substrates. Molecules of a specific length may serve as molecular wire-like transmitters in a specifically patterned nano-electronic array. Consequently, these precisely controlled length compounds are of great significance in their own right.

The detailed characterization of precisely defined materials is often far easier than characterization of the polydisperse homologues. NMR spectroscopic

details are usually more easily resolved than with randomly distributed polymer samples; however, even on the well-defined systems, the ability to make an exact assignment becomes increasingly difficult with larger structures. With the advances in matrix assisted laser desorption ionization mass spectrometry (MALDI-MS), molecular ions of synthetic polymers up to the 200 000 Da range can be obtained.⁶ This data has proved invaluable for the characterization of large well-defined structures.

General methods of preparation

The major obstacle in studying precisely defined oligomers and polymers lies in the difficulty of their isolation in pure form. Early work often focused on fractionation methods for obtaining oligomers or small polymers. One would start with a difunctional monomer and carry out standard polymerization reactions; however, the reaction times were shortened and the reaction temperatures were lowered to maximize the formation of the lower molecular weight species. The yield of a desired product was often exceedingly low while separation methods usually proved to be inadequate for the preparative fractionations needed. Similarly, one could start with polymeric material and carry out a degradation process to generate oligomeric compounds. As before, the inadequacy of the requisite fractionation process inhibits the utility of this approach.

More recently, modern synthetic organic and organometallic methodologies are proving to be extremely powerful for the direct acquisition of the desired compounds by stepwise approaches. The stepwise approaches can take several forms. A monofunctional monomer can be added, successively, to the end of a growing chain. After the addition of each monomer unit, the material is usually purified, the new end refunctionalized, and another monomer unit

attached to the end of the chain. An analogous segmented synthetic procedure can be utilized where oligomers of known length are added to the end or ends of a chain with the same purification and end group refunctionalization being needed after each step⁵. In this segmented procedure, rather than having only one unit growth per iteration, the oligomeric chain can grow by several monomer units per iteration. Purifications can also be simpler here since the differences in size between the reacted segments and the unreacted segments are often several monomer units in length. Even with this approach, however, there reaches a point where the differences in the polymeric homologues are not sufficient to permit facile separation from each other. Moreover, low solubility of the larger intermediates is often a problem. As expected, the solubility problem often manifests itself at very early stages during the preparation of rigid rod compounds.

An extrapolation of this stepwise approach has been in the development of solid-phase support-based oligomer synthesis; a method pioneered by Merrifield for the preparation of oligopeptides⁷. In this approach, monomer units are bound, via a covalent linkage, to an insoluble polymer support such as poly(*p*-chloromethylstyrene) or borosilicate glass beads. The free end of the polymer-supported unit is then activated and coupled to a new unit that is dissolved in a suspension of the polymer-supported material. After reactivation, new units are successively added to the ends of the previous unit. Complete reaction growth emanating from all oligomeric chains is critical or else some of the growing chains will be shorter than the others. One of the major advantages of this solid-phase supported method is that vast excesses of monomeric reagents can be added to help insure that all chain ends properly activate and affix a new unit. The excess reagents are easily removed by filtration and washing of the solid-phase. In many cases, the solid-phase method can easily be applied to a continuous flow

system with automation. Another method to insure that nearly all growing chains will have the same length and sequence is to use a second reagent that will irreversibly block the end of the chains that did not affix the new end group. In this way, one will not continue to grow off a chain end that is deficient in chain length. This is useful since, ultimately, it is far easier to separate two compounds of large size differences. For example, a tetramer is easily separated from an 18-mer while a 17-mer can be very difficult to separate from an 18-mer. Once the desired oligomeric sequence has been synthesized, the chains are cleaved from the support by some chemical or photochemical method to afford the desired, near uniform oligomers. If possible, purification at this point is needed to remove the irreversibly blocked shorter chains. Segmental growth can also be applied to solid-phase synthetic methods.

A newer approach, first described by Whiting, involves the use of an iterative divergent/convergent approach (Scheme 1)⁸. A monomer M, with inactive end groups X and Y, is divided into two portions. In one portion, the end group X is activated by conversion to X'. In the second portion, Y is activated by conversion to Y'. The two portions are then brought back together to form the dimer XMMY with loss of X'Y'. Since the same end groups that were present in the monomer are now present in the dimer, the procedure can be repeated with a doubling of molecular length at each iteration. The advantages of this approach are that the molecular length grows very rapidly and incomplete reactions yield unreacted material that is half the size of the desired material. Hence, purification at each step is far simpler since separation involves, for example, an octamer from a 16-mer. This iterative divergent/convergent approach is, therefore, particularly attractive.

Finally, genetic engineering techniques, or recombinant DNA methods, have been used for the construction of peptides of precisely known length,

constitution, and stereochemistry. These are best described as enzymatically controlled stepwise oligomer syntheses. These methods are becoming increasingly important in materials science since multigram quantities of specifically desired peptides can now be synthesized⁹.

Specific classes and applications of precisely controlled systems

Saturated hydrocarbons

Linear high density polyethylene (unbranched material) is of significant industrial importance, and since it represents the simplest of the organic polymers, it has been the subject of substantial work in polymer physics. Phase transition studies could be facilitated by the investigation of a series of well-defined oligomeric and polymeric structures, namely the *n*-paraffins⁸. Large amounts of work were done on the fractionation and step-wise synthetic approaches to these compounds, however, the iterative divergent/convergent approach was far more successful (Scheme 2). Starting with the C₁₂ ω-bromoacetal, half of the material was converted to the phosphonium salt while the other half was hydrolyzed to liberate the aldehyde. The Wittig reaction produced the dimeric species. Iteration of this approach afforded the C₂₄, C₄₈, and even the C₉₆ analogs. The final bromide, aldehyde, and alkene moieties were reductively removed to form the *n*-paraffins. Attempts to produce the C₁₉₂ material were met with limited success due to the insolubility of the intermediates, inseparable impurities, and difficulties in characterization. Thus, regardless of the approach, these three problems are eventually manifested during the synthesis of precisely controlled length polymers.

Oligoamides, oligopeptides and oligonucleotides

The step-wise synthesis of linear monodisperse oligoamides (nylons) and oligopeptides has been accomplished with compounds containing up to 175 chain atoms¹⁰. For example, ω -amino acids have been coupled via phosphite intermediates with activation and amide bond formation being achieved in a single pot⁵. Similar approaches have been used to make oligopeptides⁵.

Solid-phase procedures are most commonly used for the synthesis of oligopeptides¹¹ and oligonucleotides¹². Solid-phase methods form the basis of the Merrifield approach to the automated production of oligopeptides. A recent example of nanotube construction based on a self-assembling cyclic peptide architecture serves as an excellent demonstration of the state-of-the-art methods for controlled oligomer synthesis being applied to novel supramolecular assemblies. It features an eight-residue cyclic peptide, *cyclo*[-(D-Ala-Glu-D-Ala-Gln)₂-], that can adopt a low energy ring-shaped conformation in which subunits participate in backbone-backbone intermolecular hydrogen bonding to create a desired hollow tubular core structure (Figure 1)¹³. Possible applications of the tubular bundles include catalysis, inclusion chemistry, molecular electronics, and molecular separation technology.

In utilizing recombinant DNA techniques for peptide synthesis, the primary amino acid sequence of the desired polymer must first be encoded into a complementary sequence of DNA that is synthesized by either enzymatic ligation or solid-phase synthesis. The synthetic sequence is inserted into a plasmid and incorporated into an appropriate expression vector, which is then transferred to a host organism, frequently bacterial, for protein expression by fermentation techniques. Isolation and purification follows, often providing up to multigram quantities of the desired oligopeptides. Modification of materials properties by, for example the manipulation of secondary structures such as α -helices, β -strands and reverse turns in order to influence chain folding, is of current interest.

Moreover, incorporation of unnatural amino acids greatly expands the potential for structural modifications. Certainly, such methods will be further refined for biological applications as well as the construction of novel materials¹⁴.

Almost all synthetic oligonucleotides are prepared by solid phase phosphoramidite techniques. The entire process involves (1) affixing a nucleoside to a borosilicate glass support, (2) deprotecting the sugar to provide a free 5'-hydroxyl moiety, (3) addition of an excess of the second nucleotide, protected at the 5'-hydroxyl position to prevent self-polymerization and activated at the 3'-phosphate to facilitate condensation and thus formation of the support-bound dimer, (4) washing to remove the excess unreacted second nucleotide (5) capping of the unreacted mononucleotides to make them inert to further couplings, (6) repeating of the process until the desired sequence is synthesized, (7) cleaving the oligomer from the support, and (8) finally purifying the material, usually by a chromatographic technique. Remarkably, an oligonucleotide can be rapidly auto-assembled, in less than 8 minutes per nucleotide addition, to afford up to a 50 residue oligonucleotide in a single day¹². Undoubtedly, this is a highly refined and optimized approach to complex oligomers and polymers of precisely controlled length and constitution.

Fully conjugated compounds

Conjugated monodisperse oligomers and polymers represent an important class of new systems that have attracted widespread interest. These are serving as useful models for electronically and photonically (linear and nonlinear optics) important polymers, they may act as potential molecular-sized wires in the study of molecular electronics, and they can provide rigid frameworks for the construction of unique organic supramolecular assemblies.

Step-wise repetitive Diels-Alder reactions have been used to prepare linear semi-ladder rigid rod molecules that are 75 Å long (Figure 2a)¹⁵.

Step-wise approaches have been used to make interesting families of oligo(*o*-phenylene-ethynylene)s by Pd/Cu mediated couplings of aryl iodides and terminal alkynes (Figure 2b)¹⁶. Thermolysis of these compounds yielded oligo(acene)s while the spectroscopic study of the family of compounds provided insight into the electronic conjugation length of the extended π -systems.

Several studies on precisely controlled oligo(arylene vinylene)s (Figure 2c) and oligorylenes (Figure 2d) have been carried out to better understand the interplay between π -conjugation and the electronic and optical properties in polymers¹⁷.

The extraordinary proton-doped conducting properties of polyaniline have been probed utilizing phenyl-capped octaaniline, prepared by a segment approach, from tetraaniline and dihydroxydihydroterephthalic acid (Scheme 3)¹⁸. Remarkably, the monodisperse octaaniline, upon doping, exhibited the same conductivity as polyaniline. This suggests that the charge carriers on polyaniline are localized on just a few aniline units and that an intermolecular mechanism must be operating for charge transport.

The nonlinear optical, chromotropic (color changing), and dichroic properties of polydiacetylenes, that is conjugated polyeneyne structures, have been of considerable interest. A stepwise synthesis of the series of well-defined structures shown in Figure 2e permitted (1) a direct comparison between typical nondegenerate ground state conducting polymers with a polyeneyne and (2) an analysis of the polydiacetylene's electronic and photonic properties intrinsic to the polyeneyne backbone¹⁹.

In a similar study, we have used standard couplings reactions to synthesize families of homogeneous, soluble, substituted α -oligothiophenes (Figure 3). We

studied the linear optical²⁰, nonlinear optical²¹, and electronic properties²² of the oligomers. By comparison of the UV-visible spectroscopic characteristics of the oligomers with the spectra of the analogous polymers, it was determined that, in solution, electrochemically prepared poly(3-alkyl- α -thiophene) effectively has only 6-7 contiguous conjugated α -thiophene units. However, in the solid state, the conjugation path in the polymer is much longer, probably due to crystalline ordering²⁰. The third order nonlinear optical studies, by third-harmonic generation, on the family of soluble α -oligothiophenes corroborated well with the results obtained on the polymeric systems while refuting data that had been obtained on the far less soluble unsubstituted oligothiophenes²¹. The electronic properties of the soluble thiophenes were most informative. These soluble thiophene oligomers with three or more units can be electrooxidized stepwise at room temperature to give, sequentially, both the radical cation and dication forms. This was in contrast to the previous conclusion that conducting and conjugated polymers are expected to be oxidized in one broad single step²². Moreover, the study demonstrated that previous assignments of electronic transitions were inappropriate. Correlation of the energy of the electronic transitions of the oxidized oligomers permitted us to estimate the delocalization length of the radical cation (12 units) and the dication (10 units) in the corresponding polymer²².

Analogous α -oligothiophenes of precisely controlled length have been synthesized up to the 11-mer utilizing Lawesson's reagent for the thiophene ring formations (Scheme 4)²³. The values of λ_{max} increase along the oligomeric series, and even between the nonamer and 11-mer, the values of λ_{max} continued to rise. Additionally, the doped conductivity of the 11-mer was similar to that of the doped polythiophenes, inferring that the effective conjugation length in the

polymer is not much more than 11 units. However, doping induced coupling of the oligomer was not ruled out.

Recently, the construction of molecular electronics based computational instruments has attracted the attention of many because the ultimate computational system would consist of logic devices that are ultra dense, ultra fast, and molecular-sized. Even though state-of-the-art nanopatterning techniques allow lithographic probe assemblies to be engineered down to the 100 Å gap regime, the issue of electronic conduction based upon single or small packets of molecules has not been addressed and the feasibility of molecular electronics remains theoretically controversial. In an attempt to assess the possibility of molecular wire conduction by spanning the 100 Å probe gaps with small packets of molecules, we recently described the synthesis of α -thiophene-alkynylene oligomers. Our approach to such a molecular framework involved the rapid iterative divergent/convergent approach using, successively, the same three sets of reaction conditions (Scheme 5)²⁴. The monomer through 16-mer have been characterized spectroscopically. While the tetramer and octamer afforded molecular ions by direct exposure via electron impact mass spectrometry, neither this method nor fast atom bombardment or electrospray mass spectrometry sufficed for obtaining a molecular ion of the final 16-mer. However, MALDI-MS did afford an M+1 peak and this information proved to be most important for the definitive characterization^{6,24}. We used a similar method to prepare *p*-phenylene-alkynylene oligomers (Figure 4a)²⁵. The linear phenylene-alkynylene arrangement should minimize undesired conformational movement during adhesion and testing between nanofabricated probes. Additionally, the arylene-ethynylene oligomers were easily functionalized at the ends to serve as "molecular alligator clips" that might be required for surface contacts to metal probes for molecular electronics study. For example, we have functionalized the

ends of the oligomeric systems with thiol moieties, shown in protected form (Figure 4b), for adhesion to gold probes by self-assembly methods²⁶. We have also synthesized isonitrile end groups for adhesion to tungsten probes. Thus, the iterative divergent/convergent approach permitted both the facile construction of the potential molecular wires as well as providing compounds with ends that could be readily functionalized.

In addition to these conjugated molecules serving as potential molecular wires, the optical and chromatographic properties proved to be most intriguing. An optical saturation or near saturation of the systems occurred by the octamer stage so that doubling the conjugation length to the 16-mer caused little or no change in the position of the absorbance maximum (Figure 5a)^{24,25}. The results of the size exclusion chromatography (SEC) are shown in Figure 5b and compared with the actual molecular weights of the oligomers. SEC is not a direct measure of MW, but a measure of the hydrodynamic volume. Thus, by SEC using randomly coiled polystyrene standards, the number average molecular weights (M_N) of rigid rod polymers are usually greatly inflated relative the actual molecular weights. Accordingly, the SEC recorded M_N values of the octamers and 16-mers were much greater than the actual molecular weights. Also, as we would predict, the monomer, dimer, and tetramer had M_N values that were reasonably close to the actual molecular weights (slope ~ 1.0 in Figure 5b) because they are in the low MW region, prior to significant polystyrene coiling. In all cases, the SEC-determined values of $M_w/M_N = 1.02-1.07$. Thus this plot can serve as a useful calibration chart for very rigid linear oligomers as they compare to polystyrene standards by SEC^{24,25}.

In a related study directed toward the construction of molecular electronic devices, we synthesized molecules with potentially addressable "on" and "off" states. The orthogonally fused conjugated oligomers are of precisely controlled

length and molecular constitution for electronic testing. First, the spiro cores were constructed²⁷, and then all four branching arms were added in a single operation (Figure 6a-c)²⁸. Electrochemically, we could independently observe the formation of the mono(radical cation), bis(radical cation), radical-cation(dication), and bis(dication) which indicates that, under unperturbed conditions, there is no cross-communication between the upper and lower segments, a prerequisite for the device capability²⁹. Addressing is proposed by considering a six probe assembly; a probe at each of the four trimethylsilyl ends, a probe above the central spiro core moiety, and a probe below the central spiro moiety³⁰. Instrument-induced electron removal (doping) from the top branch would permit facile conduction in the top segment while leaving the bottom segment unchanged (state 1). At a certain threshold potential (perturbation) across the spiro bridge, an electron would tunnel from the lower chain to upper chain, via the spiro core, to produce a doped (conducting) lower chain and a neutral upper chain (state 2). The two states would then be addressable based on the potential across the spiro bridge, thus creating a device. From such devices or simple two-state systems, logic gates could be formed³⁰. Note that no such six probe array, at these dimensions, is presently available by nanopatterning techniques, though lithographic and nonlithographic patterning methods will probably approach this capability within 3-5 years³¹.

Conjugated oligomeric structures that are terminated by porphorins are attracting widespread attention for use in (1) photosynthetic reaction centers such as light harvesting antenna, (2) stabilization of charge separation, and (3) sequential electron transfer³². An interesting porphyrin terminated phenylene vinylene oligomer was synthesized by a segmented approach involving cheletropic-derived extrusion of SO₂ to afford the vinylene moieties (Figure 6d)³³.

Another fascinating utilization of rigid, conjugated, precisely defined oligomeric structures is for the construction of supramolecular assemblies. Oligo(*m*-phenylene-ethynylene)s, the monomer to 16-mer, have been prepared by the iterative divergent/convergent approach³⁴. Analogous structures were then converted into phenylene-ethynylene macrocycles by activation of the ends (aryl iodide and terminal alkyne) and intramolecular coupling with a Pd/Cu catalyst under dilute conditions (Figure 6e).³⁵ If we consider this macrocycle as a modular unit, there is the hope of using such units for the programmed assembly of molecular materials. This may be accomplished by utilizing the constitution of the individual fragments to control the condensed phase organization through the summation of non-covalent interactions; an approach analogous to the forming of structures using building blocks held together by frictional forces that are dependent upon good facial overlap (Figure 6f)³⁶. Ultimately, the target is the rational design of new materials such as organic crystals and tubular mesophases.

Following solid-phase peptide construction methods, the novel synthesis of oligo(phenylene-ethynylene)s has been achieved on polystyrene supports³⁷. This method has been used in conjunction with the iterative divergent/convergent approach to rapidly construct oligomers through the 16-mer in length.

Miscellaneous oligomeric and polymeric structures

As the field of potential molecular machinery is capturing the imagination of chemists, structures based on linear rigid rod molecules that could assemble, either free-floating or surface-anchored, are being synthesized by stepwise and fractionation approaches. These compounds are described as potential early stage novel building blocks for nanoarchitected tinkertoy-like suprastructures. Required in the construction is the synthesis of very rigid materials of precisely defined length and constitution. To that end, non-conjugated rigid-rod oligomers

based on *p*-carboranes have been constructed (Figure 6g)^{38,39}. Likewise, non-conjugated structures based on [*n*]staffanes have also been isolated by gradient sublimation (Figure 6h)⁴⁰.

Polyurethanes and polyether blocks of precisely controlled length and constitution have been synthesized in a stepwise approach to create multiphase polymer systems with unique phase structures and properties⁴¹. The chain architecture permitted both the control and the extent of the phase separation, the type of self-organization, and the macroscopic structural order in the multiphase polymeric systems.

Summary and future directions

Step growth oligomers and polymers will continue to be of interest as easy-to-study precise analogues of their higher polymeric forms. Families of oligomers and small polymers will be synthetic targets in order to predict and enhance the understanding of the physical, optical, and electronic properties in the corresponding polymers. In addition to serving as models, these oligomeric structures are becoming more important in their own right; for example, in the electronics arena as nanoscale devices, and in the biological and materials area for supramolecular assembly construction. As more applications of precisely defined structures become recognized, solid-phase automated methods will continue to be the synthetic strategies of choice. This is especially true in light of the recent advances in combinatorial syntheses where large numbers of varying structures can be simultaneously constructed⁴². However, if the large-scale production (multi-kilos) of these well-defined structures will be required, solid-phase methods may be limited due to the volumes of support-phase needed; a limitation that has been observed in the solid-phase-based commercial production of oligopeptides. Finally, the advances in the synthesis and utility of step growth

oligomers and polymers of precisely controlled length and constitution are made possibly by a rapid evolution and improvement in new synthetic organic and organometallic methodologies as well as in improved methods of chemical analysis.

Acknowledgments

Support of our program on the synthesis of precisely defined oligomers and polymers has been provided by the Office of Naval Research, the National Science Foundation (EHR-91-08772, DMR-9158315), and the Advanced Research Projects Agency.

References

- 1 Wirth, H. O., Herrman, F. U. and Kern, W. (1964) *Makromol. Chem.* 80, 120
- 2 Fréchet, J. M. J. (1994) *Science* 263, 1710
- 3 Tomalia, D. A. (1993) *Aldrichimica Acta* 26(4), 91
- 4 Uglea, C. V. and Negulescu, I. I. (1991) *Synthesis and Characterization of Oligomers*, CRC Press
- 5 Rothe, M. (1991), in *Chemistry and Physics of Macromolecules*, (Fischer, E. W., Schulz, R. C. and Sillescu, H. eds), pp 39-60, VCH
- 6 Creel, H. S. (1993) *Trends in Polym. Sci.* 1, 336
- 7 Merrifield, R. B. (1963) *J. Am. Chem. Soc.* 85, 2149
- 8 Ignier, E., Paynter, O. I., Simmonds, D. J., and Whiting, M. C. (1987) *J. Chem. Soc., Perkin Trans. I* 2447
- 9 Tirrell, D. A., Fournier, M. J. and Mason, T. L. (1991) *MRS Bulletin* 16, 23
- 10 Rothe, M. and Mazanek, J. (1972) *Tetrahedron Lett.* 3795
- 11 *Techniques in Protein Chemistry II* (1991), (Villafranca, J. J., ed), Section III, pp 209-250, Academic Press
- 12 Brown, T. and Brown, D. J. S. (1991), in *Oligonucleotides and Analogues*, (Eckstein, F., ed), pp 1-23, Oxford University Press
- 13 Ghadiri, M. R., Granja, J. R., Milligan, R. A., McRee, D. E., and Khazanovich, N. (1993) *Nature* 366, 324
- 14 Tirrell, D. A., Fournier, M. J. and Mason, T. L. (1991) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 32(3), 704
- 15 Kenny, P. W. and Miller, L. L. (1988) *J. Chem. Soc., Chem. Commun.* 84
- 16 Grubbs, R. H. and Kratz, D. (1993) *Chem. Ber.* 126, 149
- 17 Scherf, U. and Müllen, K. (1992) *Synthesis* 23
- 18 Lu, F.-L., Wudl, F., Nowak, M. and Heeger, A. J. (1986) *J. Am. Chem. Soc.* 108, 8311

- 19 Wudl, F. and Bitler, S. P. (1986) *J. Am. Chem. Soc.* 108, 4685
- 20 Tour, J. M. and Wu, R. (1992) *Macromolecules* 25, 1901
- 21 Cheng, L.-T., Tour, J. M., Wu, R. and Bedworth, P. V. (1993) *Nonlinear Optics* 6, 87
- 22 Guay, J., Kasai, P., Diaz, A., Wu, R., Tour, J. M. and Dao, L. H. (1992) *Chem. Mater.* 4, 1097
- 23 ten Hoeve, W., Wynberg, H., Havinga, E. E. and Meijer, E. W. (1991) *J. Am. Chem. Soc.* 113, 5887
- 24 Pearson, D. L., Schumm, J. S. and Tour, J. M. (1994) *Macromolecules* 27, 2348
- 25 Schumm, J. S., Pearson, D. L. and Tour, J. M. *Angew. Chem. Int. Ed. Engl.* (in press)
- 26 Schumm, J. S., Jones, L., II, Pearson, D. L., Hara, R. and Tour, J. M. (1994) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 35(2), 687
- 27 Tour, J. M., Wu, R. and Schumm, J. S. (1990) *J. Am. Chem. Soc.* 112, 5662
- 28 Tour, J. M., Wu, R. and Schumm, J. S. (1991) *J. Am. Chem. Soc.* 113, 7065
- 29 Guay, J., Diaz, A., Wu, R. and Tour, J. M. (1993) *J. Am. Chem. Soc.* 115, 1869
- 30 Aviram, A. (1988) *J. Am. Chem. Soc.* 110, 5687
- 31 *Nanostructures and Mesoscopic Systems* (1992), (Kirk, W. P., Reed, M. A. eds.), Academic Press
- 32 Lin, V. S.-Y., DiMugno, S. G. and Therien, M. J. (1994) *Science* 264, 1105
- 33 Ono, N., Tomita, H. and Maruyama, K. *J. Chem. Soc. Perkin Trans. I* (1992) 2453
- 34 Zhang, J., Moore, J. S., Xu, Z. and Aguirre, R. A. (1992) *J. Am. Chem. Soc.* 114, 2273

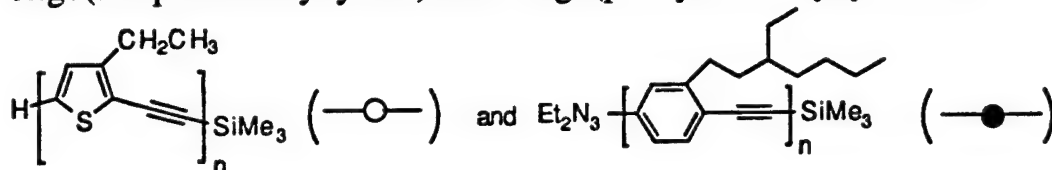
- 35 Zhang, J., Pesak, D. J., Ludwick, J. L. and Moore, J. S. (1994) *J. Am. Chem. Soc.* 116, 4227
- 36 Moore, J. S., Zhang, J., Wu, Z., Venkataraman, D., and Lee, S. (1994) *Macromol. Symp.* 77, 295
- 37 Young, J. K., Nelson, J. C. and Moore, J. S. *Polym. Prepr.* (1994) (*Am. Chem. Soc., Div. Polym. Chem.*) 35(2), 988
- 38 Yang, X., Jiang, W., Knobler, C. B. and Hawthorne, M. F (1992) *J. Am. Chem. Soc.* 114, 9719
- 39 Müller, J., Base, K., Magnera, T. F. and Michl, J. (1992) *J. Am. Chem. Soc.* 114, 9721
- 40 Murthy, G. S., Hassenrück, K., Lynch, V. M. and Michl, J. (1989) *J. Am. Chem. Soc.* 111, 7262
- 41 Eisenbach, C. D., Heinemann, T., Ribbe, A. and Stadler, E. (1994) *Macromol. Symp.* 77, 125
- 42 Baum, R. M. (February 7, 1994) *Chemical and Engineering News* 72(6) pp 20-26

Legends for Schemes and Figures

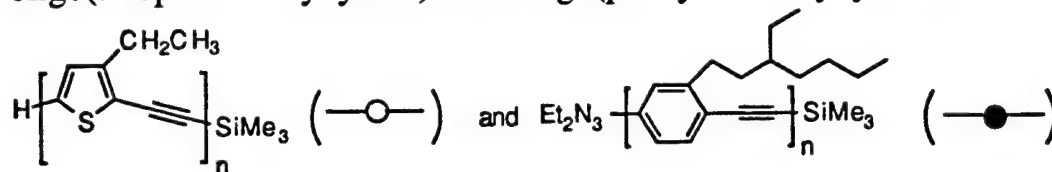
- (1) Scheme 1. Iterative divergent/convergent approach to molecular length doubling.
- (2) Scheme 2. Iterative divergent/convergent approach to *n*-paraffins.
- (3) Figure 1. Self-assembly of a nanotubular structure from cyclic oligopeptides.
- (4) Figure 2. (a) Semi-ladder rigid rod oligomer prepared by successive Diels-Alder reactions. (b) Oligo(*o*-phenylene-ethynylene) prepared in a step-wise manner by Pd/Cu coupling reactions. (c) Oligo(arylene vinylene). (d) Oligorylenes. (e) End-capped oligo(ene-yne)s for optical studies related to polydiacetylenes.
- (5) Scheme 3. Synthesis of phenyl-capped octaaniline.
- (6) Figure 3. Soluble oligothiophenes for electronic and photonic studies.
- (7) Scheme 4. Synthesis of a soluble α,α -undecathiophene.
- (8) Scheme 5. Iterative divergent/convergent synthesis of oligo(thiophene-ethynylene)s. Reagents: (a) *i*-Pr₂NLi, Et₂O, -78° to 0° C then I₂, -78° C. (b) K₂CO₃, CH₃OH, 23° C. (c) Cl₂Pd(PPh₃)₂ (2 mol %), CuI (1.5 mol %), THF, *i*-Pr₂NH, 23° C. The percentages below the arrows are the yields for each steps.

(9) Figure 4. (a) Soluble 16-mer of a linear oligo(phenylene-ethynylene). (b) Thioacetate-capped conjugated oligo(thiophene-ethynylene).

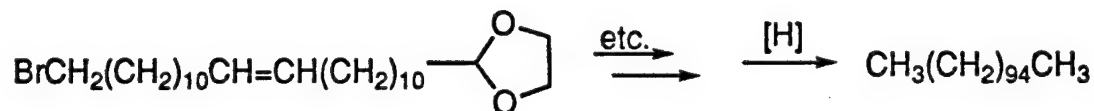
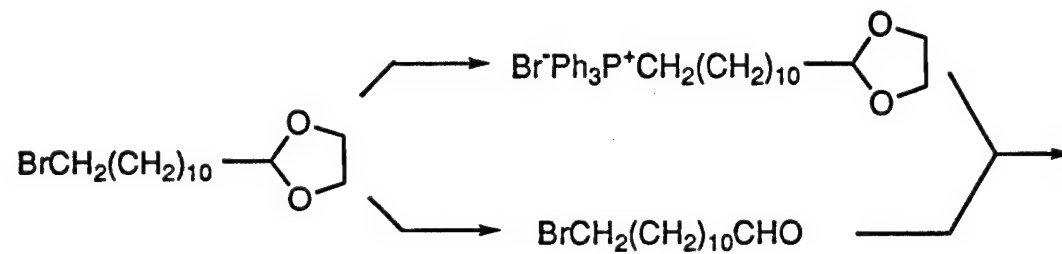
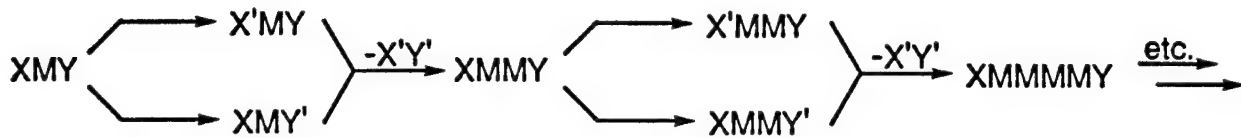
(10) Figure 5. (a) Optical absorbance maximum (λ_{\max}) in CH_2Cl_2 versus the number of units in the oligomer (n) for families of precisely-defined oligo(thiophene-ethynylene)s and oligo(phenylene-ethynylene)s.

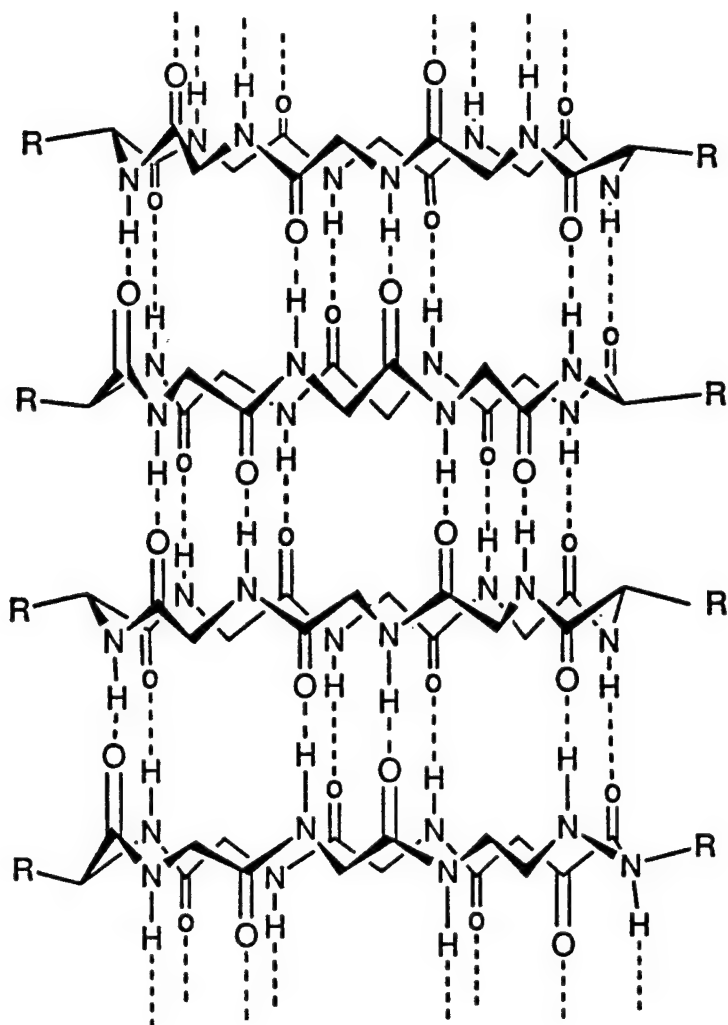


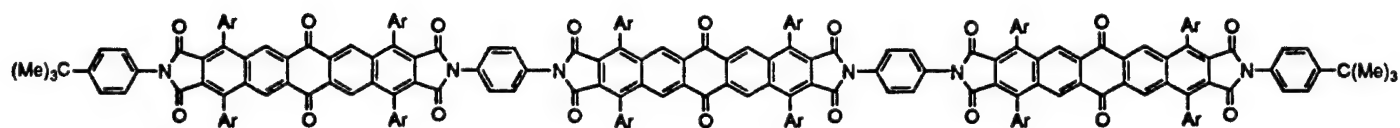
(b) Values of M_n determined by SEC in THF (relative to polystyrene standards) versus the actual molecular weights for families of precisely-defined oligo(thiophene-ethynylene)s and oligo(phenylene-ethynylene)s.



(11) Figure 6. (a-c) Orthogonally fused conjugated oligomers for molecular electronics device studies. (d) Porphyrin-terminated phenylene-vinylene oligomer. (e) Macrocyclic phenylene-ethynylene oligomer for the programmed assembly of molecular materials. (f) Conceptual approach to the condensed phase organization of molecular materials. (g) Rigid rod oligo(*p*-carboranes). (h) Rigid rod oligo[*n*]staffanes.







$Ar = p\text{-Me}_3\text{CC}_6\text{H}_4$

Fig 2a

Fig 2a

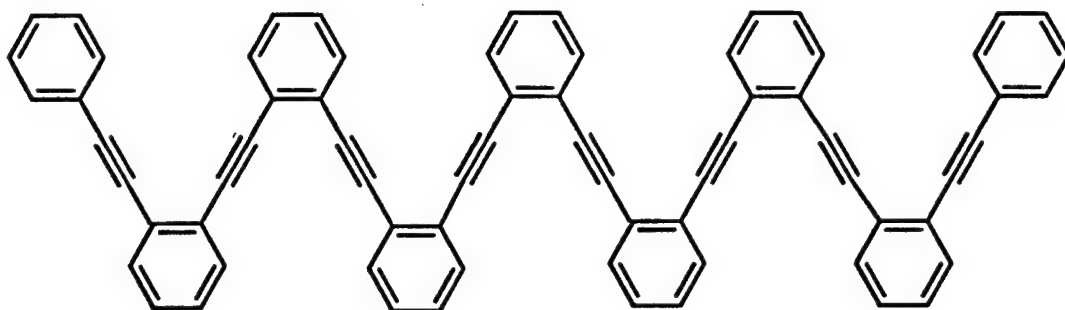


Fig 2b

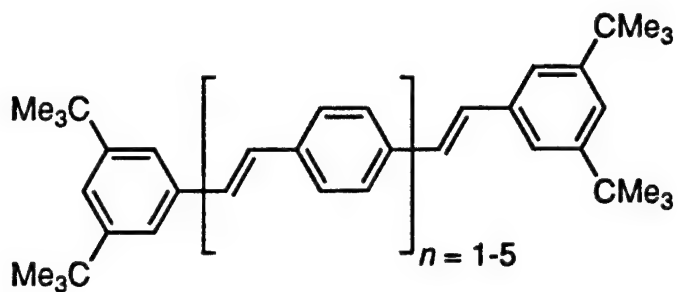


Fig 2c

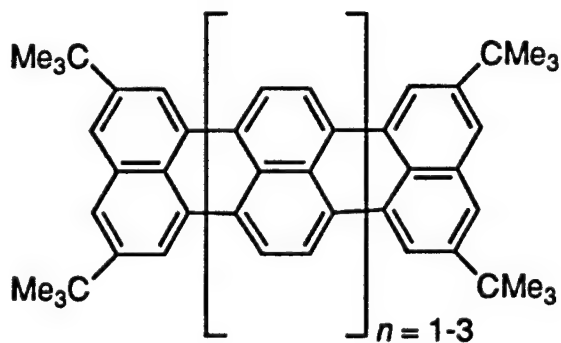
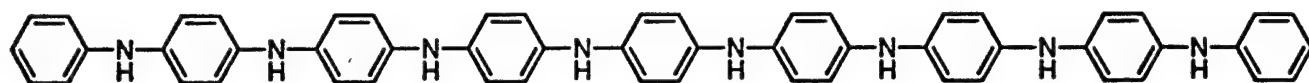
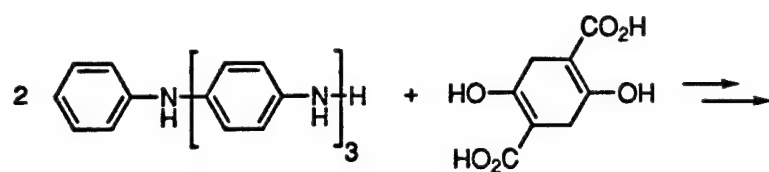


Fig 2d

Fig 2b, 2c, 2d



Scheme 3

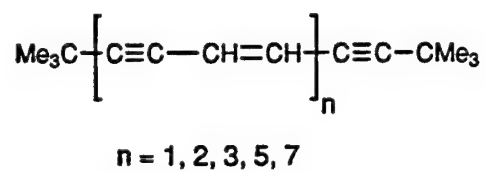


Fig 2e

Fig 2e

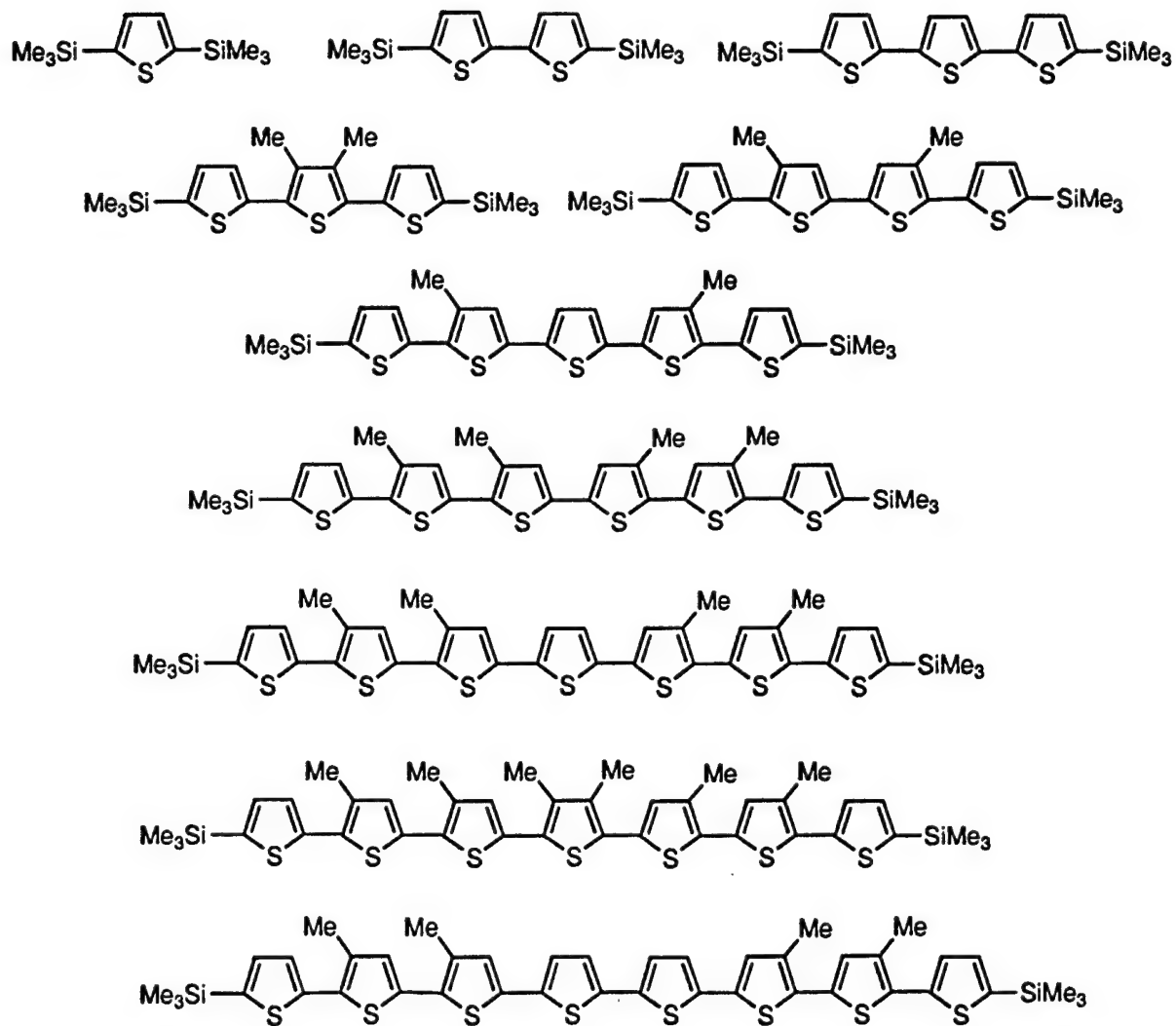
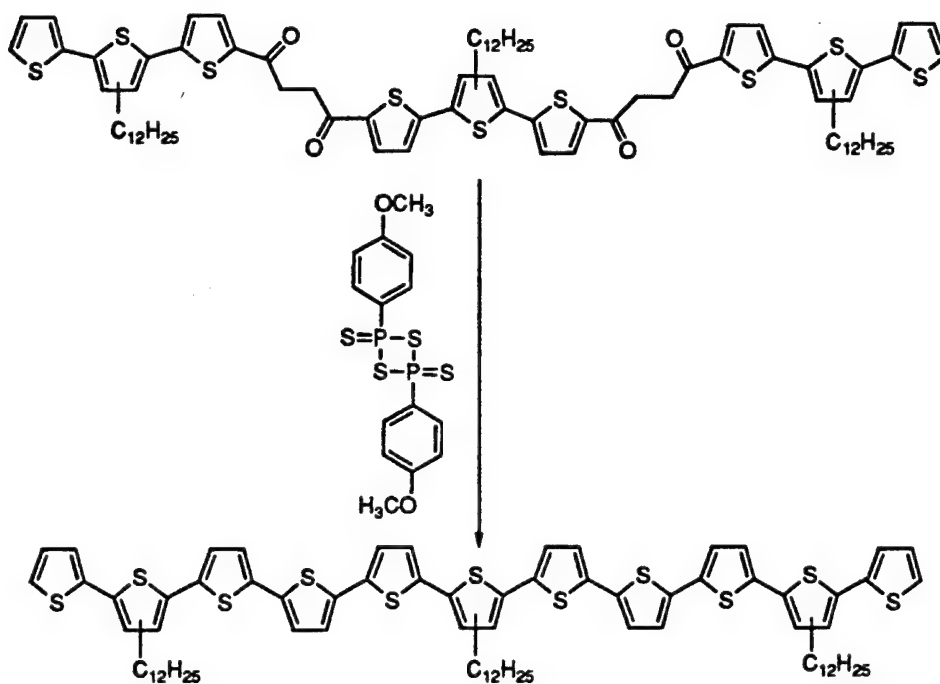
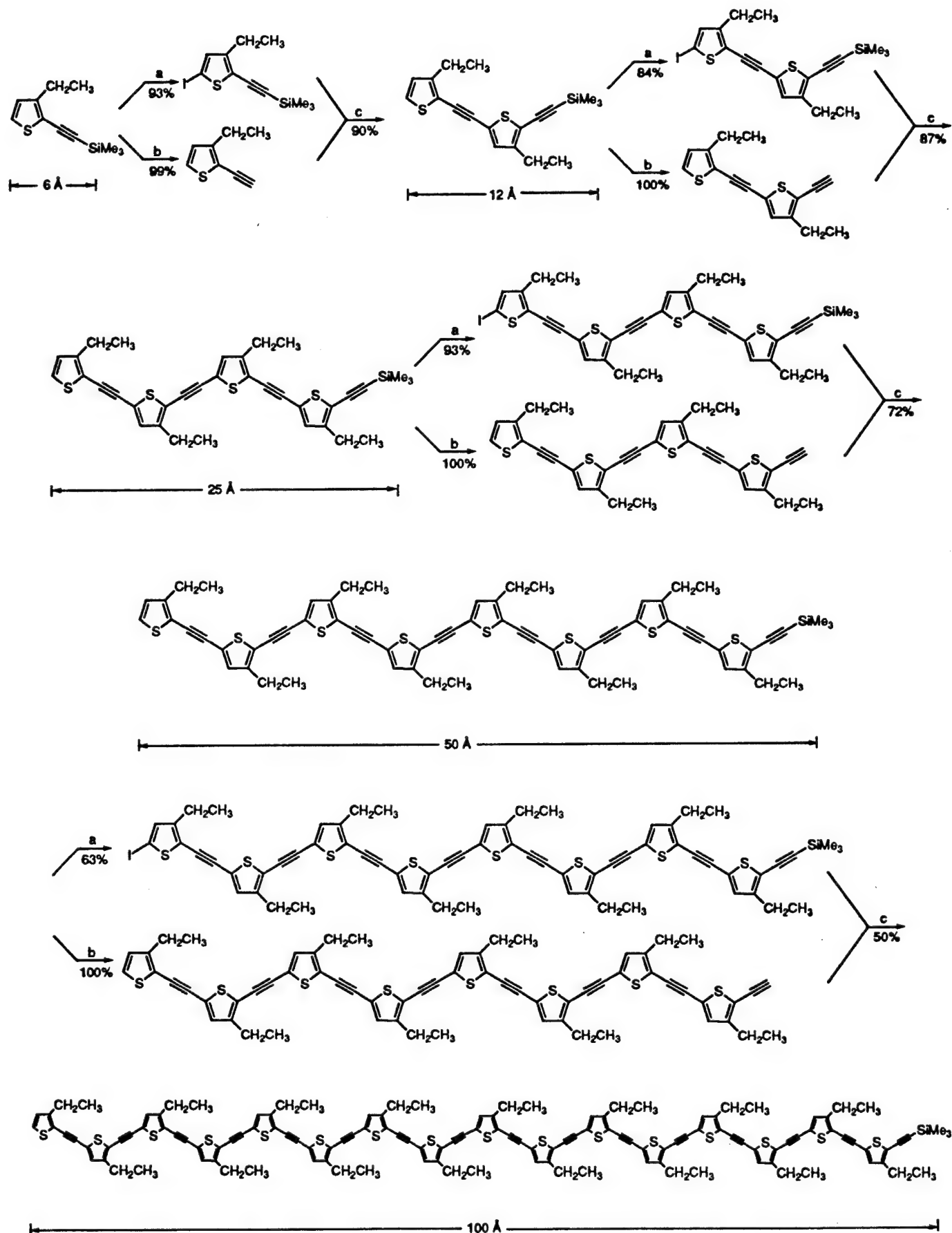


Fig 3





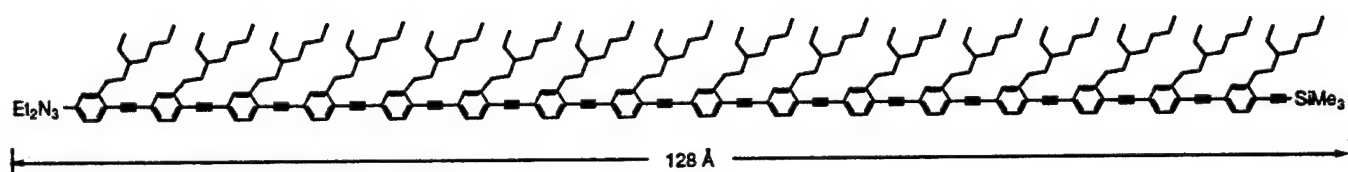


Fig 4a

Fig 4a

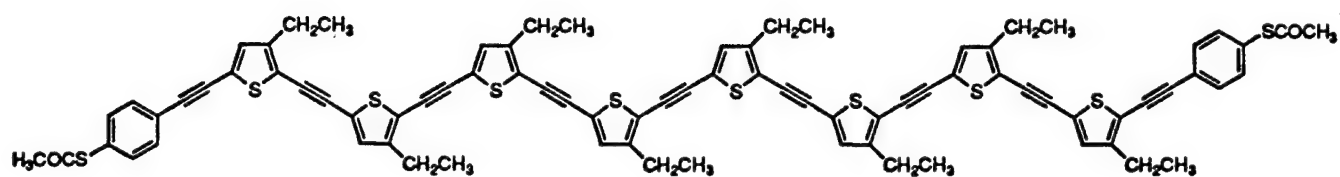


Fig 4b

Fig 4b

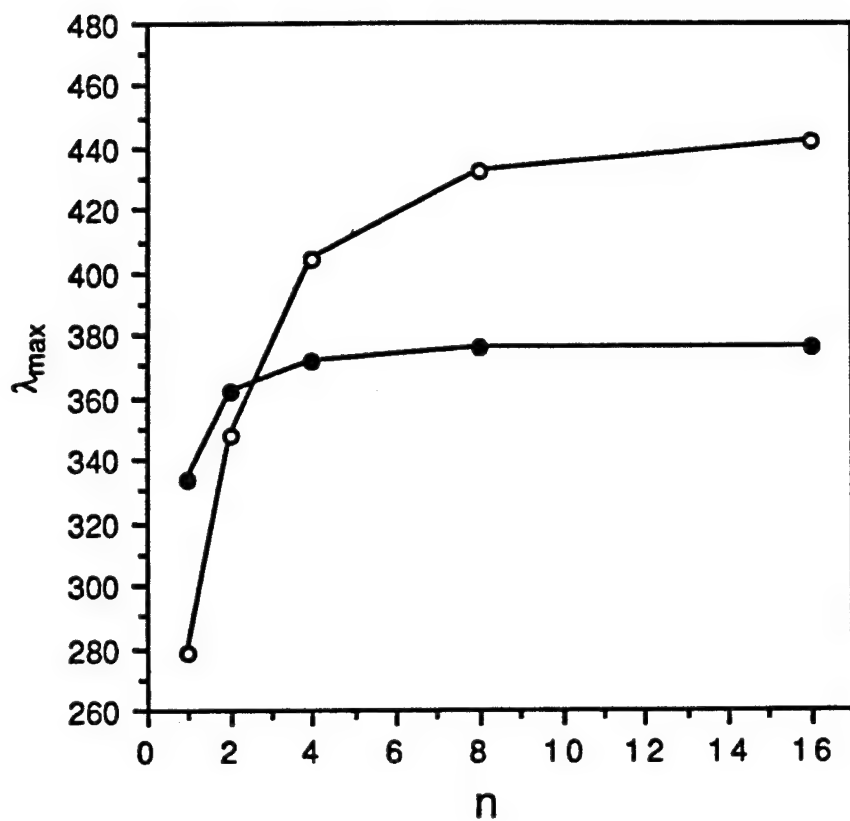


Fig 5a

Fig 5a

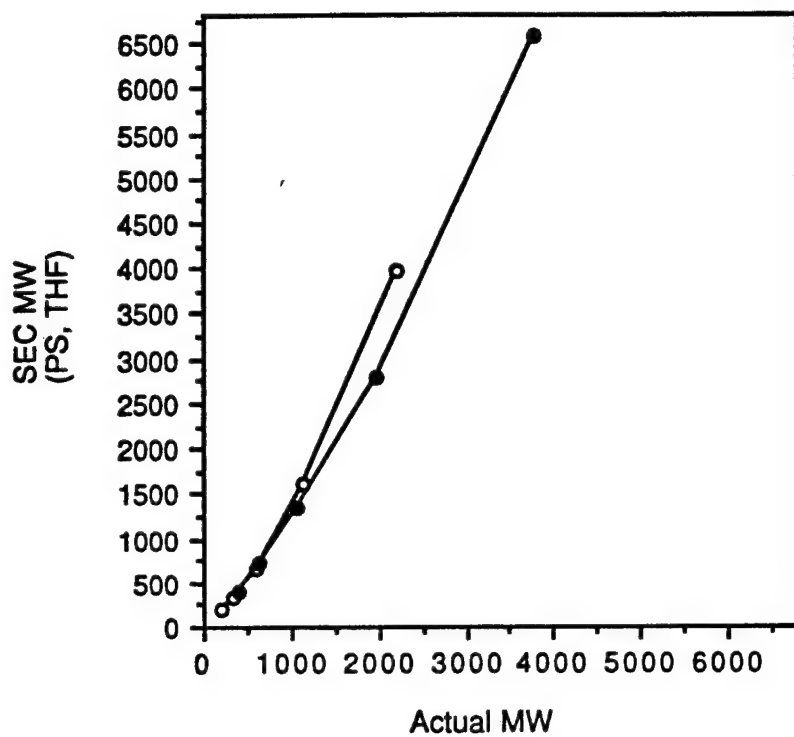


Fig 5b

Fig 5b

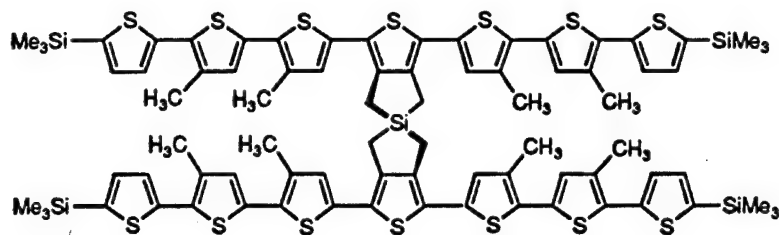


Fig 6a

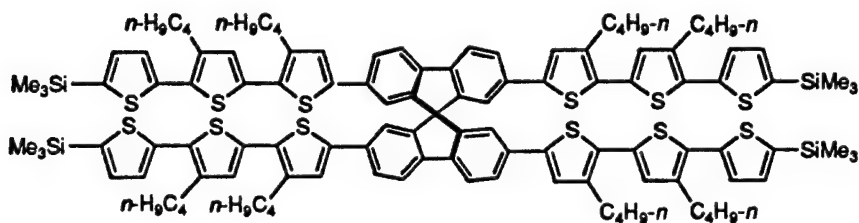


Fig 6b

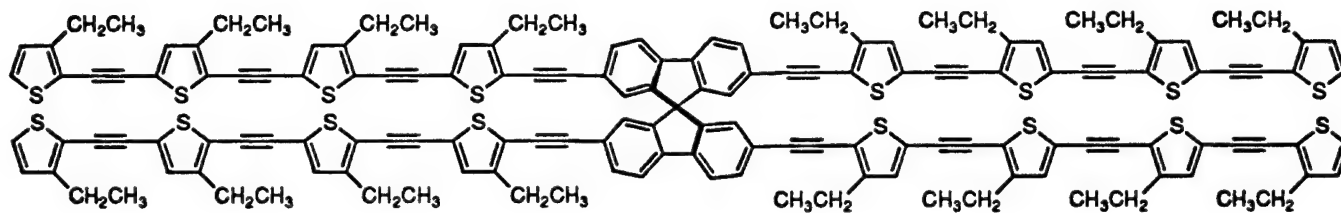


Fig 6c

Fig 6a, 6b, 6c

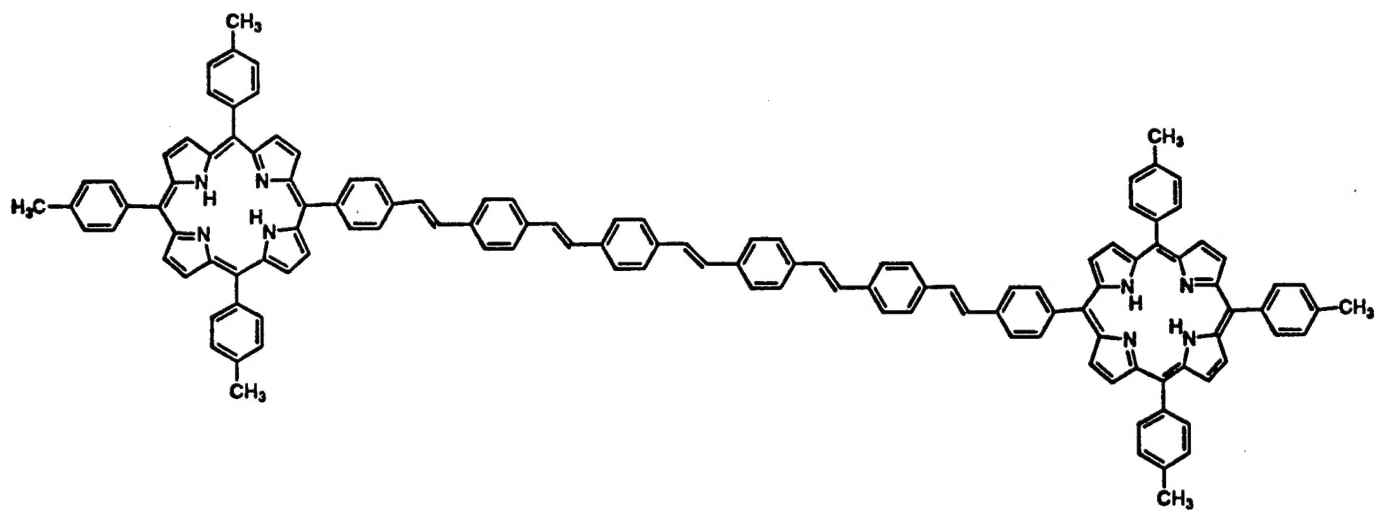


Fig 6d

Fig 6d

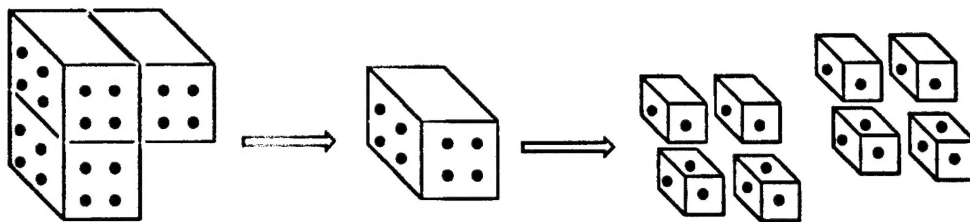


Fig 6f

Fig 6f

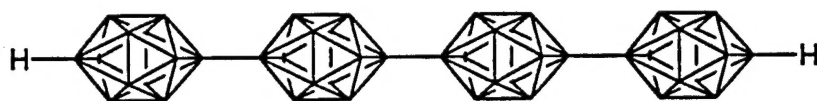


Fig 6g



Fig 6h

Fig 6g, 6h